# Symmetric and asymmetric 13-vertex bimetallacarboranes by polyhedral expansion†

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**Symmetric 4,5,2,3-$M_2C_2B_9$ 13-vertex bimetallacarboranes of cobalt and ruthenium with 14 skeletal electron pairs are afforded by reduction and metallation of 3,1,2-$MC_2B_9$ icosahedra; the symmetric species can be converted to their asymmetric 4,5,1,6-$M_2C_2B_9$ isomers by heat, but an easier route is by thermolysis of the reduced species before metallation.**

The chemistry of heteroborane clusters with > 12 vertices is an area of intense current research activity. Significant recent discoveries include the first supraicosahedral p-block metallacarborane,[1] the first 13-vertex[2] and 14-vertex[3] carboranes, the synthesis of new isomers of the 13-vertex $MC_2B_{10}$ type,[4] new homo- and heterobimetallic 14-vertex $M_2C_2B_{10}$ compounds,[5] the first 14-vertex $MC_2B_{11}$ species,[6] and the first 15-vertex heteroborane.[6] The deltahedral 13-vertex polyhedron is the $C_{2v}$-symmetric docosahedron (Fig. 1), although a henicosahedron related to this by the formal breaking of a single connectivity is known for 1,2-$C_2B_{11}$ species[2] and for certain $MC_2B_{10}$ metallacarboranes.[7] The docosahedron has one degree-four vertex (1) and two degree-six vertices (4 and 5). Given the relative electronegativities of boron, carbon and transition metals it is not surprising that the vast majority of docosahedral $MC_2B_{10}$ species have the metal in vertex 4 and one C atom in vertex 1. Moreover, in known examples of 13-vertex bimetallic $M_2C_2B_9$ compounds both metal atoms occupy vertices 4 and 5.[8–10] We now report the synthesis of $C_{2v}$-symmetric 4,5,2,3-*closo*-$M_2C_2B_9$ and asymmetric 4,5,1,6-*closo*-$M_2C_2B_9$ compounds, where $M$ = {CpCo} and {(*p*-cymene)Ru}. The symmetric species arise from reduction and subsequent metallation of 3,1,2-*closo*-$MC_2B_9$ species and provide evidence that the reduced metallacarborane has a $C_s$ symmetric structure. We identify structural differences between Wadian[11] and non-Wadian 4,5,2,3-*closo*-$M_2C_2B_9$ compounds and rationalise these in terms of the form of the HOMO of $[B_{13}H_{13}]^{2-}$.

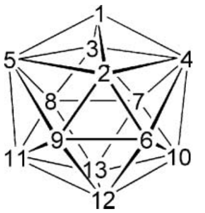

Fig. 1 The docosahedron and numbering.

Reduction of the icosahedral ruthenacarborane 3-(*p*-cymene)-3,1,2-*closo*-$RuC_2B_9H_{11}$ (**1**) (see ESI†,‡) followed by treatment with ½ equivalent of $[Ru(p\text{-cymene})Cl_2]_2$ affords 4,5-(*p*-cymene)$_2$-4,5,2,3-*closo*-$Ru_2C_2B_9H_{11}$ (**2**).† Compound **2** is clearly symmetric, revealing only one set of *p*-cymene resonances and one $CH_{cage}$ resonance in the $^1H$ NMR spectrum, and only three resonances in the $^{11}B$ spectrum. Crystallographic analysis‡ yields the structure shown in Fig. 2.

Both crystallographically-independent molecules have effective $C_{2v}$ symmetry about an axis from B1 to the mid point of B12–B13. Thus, whilst the Ru atoms occupy their expected vertices 4 and 5, unusually both carbon atoms are in degree-five sites and a boron atom occupies the unique degree-four vertex 1. An analogous structure has previously been reported for 4,5-Cp*$_2$-4,5,2,3-*closo*-$Ru_2C_2B_9H_{11}$ (**3**) by Kudinov *et al.*,[9] formed by direct insertion of an electrophilic {Cp*Ru$^+$} fragment into [3-Cp*-3,1,2-*closo*-$RuC_2B_9H_{11}]^-$. However, compound **3** is non-Wadian, having only 13 skeletal electron pairs (SEPs),[11] whereas our compound is Wadian with 14 SEPs. In view of the apparently similar structures of the two compounds in spite of their differing numbers of SEPs, we have used DFT calculations¶ to probe the nature of the HOMO of $[B_{13}H_{13}]^{2-}$ (Fig. 3), the orbital occupied in **2** but not in **3**. This orbital, of *b* symmetry, is strongly bonding with respect to the 1–2 and 1–3 edges (edges ***a***), moderately strongly bonding with respect to the 6–9 and 7–8 edges (***b***), and only very weakly bonding with respect to the 6–10, 7–10, 8–11 and 9–11 edges (***c***). In **3** the

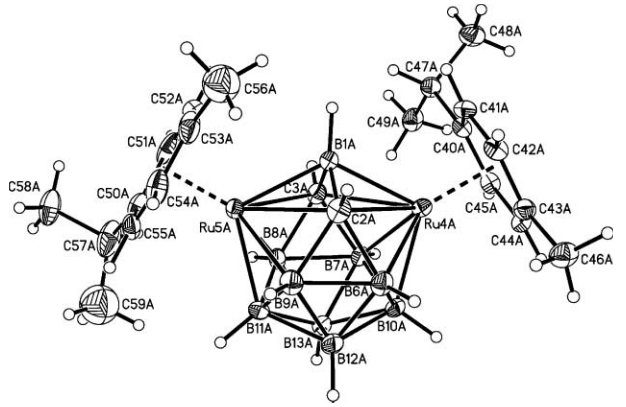

Fig. 2 Perspective view of **2** (molecule A). Average distances (Å, over both molecules) are B1–C2, B1–C3 1.561(13); B6–B9, B7–B8 1.819(5); B6–B10, B7–B10, B8–B11, B9–B11 1.812(7)§

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† Electronic supplementary information (ESI) available: Experimental procedures; computational details. See DOI: 10.1039/b703822d

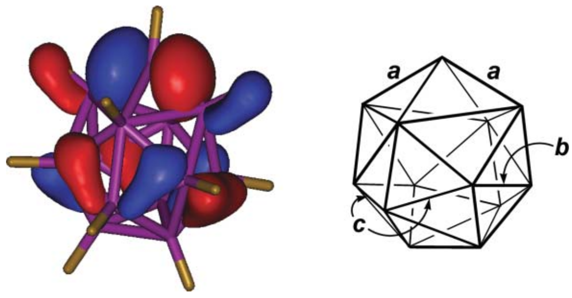


**Fig. 3** The HOMO of $[B_{13}H_{13}]^{2-}$.

average lengths of ***a***, ***b*** and ***c*** are 1.702(6), 1.851(7) and 1.798(5) Å, respectively. Thus ***a*** is substantially (0.14 Å) shorter and ***b*** modestly (0.03 Å) shorter in **3**, fully consistent with the form of the orbital.|| The change in the edges ***c*** is in the wrong sense but very small (0.01 Å). Importantly, the HOMO of $[B_{13}H_{13}]^{2-}$ is non-degenerate (necessarily so for a $C_{2v}$ point group), explaining[13] how Wadian **2** and non-Wadian **3** can have similar gross structures.

As an alternative to {(*p*-cymene)Ru}, the {CpCo} fragment is also frequently used as an isolobal surrogate for {BH}. However, reduction of 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$[14] followed by treatment with $CoCl_2$ and NaCp affords five species of which four are fully characterised.† The major product **4** and minor product **5** are both $(CpCo)_2C_2B_9H_{11}$ by mass spectrometry, but NMR spectroscopy reveals **4** to be the more symmetric of the two. Thus there is only one resonance for the Cp protons and one $CH_{cage}$ resonance in the $^1H$ NMR spectrum, and the $^{11}B$ NMR spectrum displays only three resonances, reminiscent of compound **2**, identifying **4** as 4,5-$Cp_2$-4,5,2,3-*closo*-$Co_2C_2B_9H_{11}$. A crystallographic study (Fig. 4) confirms this, but is complicated by C3 being disordered over two sites *ca.* 0.66 Å apart.‡ The weighted average length of edge ***a*** in **4** is 1.57(9) Å, consistent with **4** having 14 SEPs.

The minor product **5** has two Cp resonances of equal integral and two $CH_{cage}$ resonances of equal integral in the $^1H$ NMR spectrum, and displays six resonances in the $^{11}B$ NMR spectrum at, on average, low frequency relative to the spectrum of **4**. Compound **5** is thus the asymmetric compound 4,5-$Cp_2$-4,5,1,6-*closo*-$Co_2C_2B_9H_{11}$, previously prepared[8] by polyhedral subrogation from the ubiquitous supraicosahedral metallacarborane 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$.[15] We have confirmed the structure of **5** crystallographically (Fig. 5).‡ The unique degree-four vertex 1 hosts C1, but C6 is symmetrically disordered over positions 6, 7, 8 and 9, all of which are therefore 75% B and 25% C. Although crystallographically **4** and **5** appear similar (same space group, similar cell dimensions), the unit cells are measurably different, with an 11% difference in *a* and an 8% difference in *β*. Moreover, although there is rough agreement between the two structures in the *x* fractional coordinates of equivalent cage atoms, this does not extend to the *y* and *z* coordinates nor to the Cp ring attached to Co4.

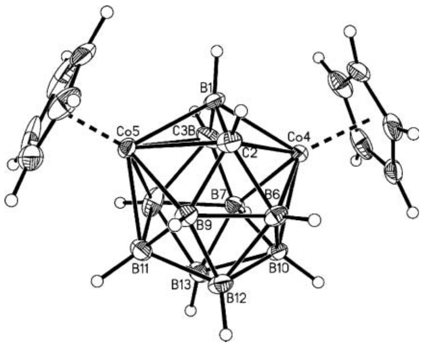


**Fig. 4** Perspective view of **4**. Only the major component (B) of the disordered atom C3 is shown for clarity. Average distances (Å) are B1–C2, B1–C3 1.57(9); B6–B9, B7–B8 1.808(4).

In **4** the cage C atoms both occupy degree-five vertices whilst in **5** one is in the preferred degree-four site. Thus it is reasonable to suggest that **5** is thermodynamically stable with respect to **4**, and, consistent with this, in refluxing THF **4** quantitatively converts to **5**. Thus it was of interest to see if the symmetrical bisruthenacarborane **2** could similarly be isomerised. No change is noted in the $^{11}B$ NMR spectrum of **2** after 48 hours at THF reflux, but at higher temperatures the resonances due to **2** gradually give way to those of a new species. At 150 °C **6** is recovered in *ca.* 80% yield after 40 hours. Its $^1H$ NMR spectrum reveals inequivalent *p*-cymene ligands, and its $^{11}B$ spectrum shows five resonances at relatively low frequency.

Crystallographic study‡ (Fig. 6) shows that **6** is 4,5-(*p*-cymene)$_2$-4,5,1,6-*closo*-$Ru_2C_2B_9H_{11}$. As in **5**, the degree-five C atom is statistically disordered over vertices 6–9, and, as with **4** and **5**, there is a correspondence between the unit cell parameters and space group of compounds **2** and **6**. However, the coordinates of corresponding atoms in **2** and **6** are not related.**††

When 1,2-*closo*-$C_2B_{10}H_{12}$ is reduced the C atoms separate[17] and the nature of the reduced species **I** can be deduced from the known structures of protonated[18] or metallated[1,15] derivatives. In **I** one C atom is a degree-three vertex. In contrast, the structure of the reduced form of 3,1,2-*closo*-$MC_2B_9H_{11}$, based on the structures found for **2** and **4**, must be that shown in **II**, with both C atoms 4-connected. However, we believe that **II** is only a kinetic isomer, and that asymmetric **5** arises from rearrangement of **II** before metallation (and not from isomerisation of **4** during work-up) since: (i) $^{11}B$ and $^1H$ spectra of pure **4** re-recorded after standing in $CDCl_3$ for 3 days show no evidence of **5**; (ii) overnight heating to reflux of reduced 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ or reduced **1** in THF before addition of the second metal results in asymmetric **5** or **6** as the only $M_2C_2B_9$ products (note that these conditions are significantly milder than those needed to produce **6** from **2**). We suggest that rearrangement of kinetic **II** occurs *via* a cascade of five

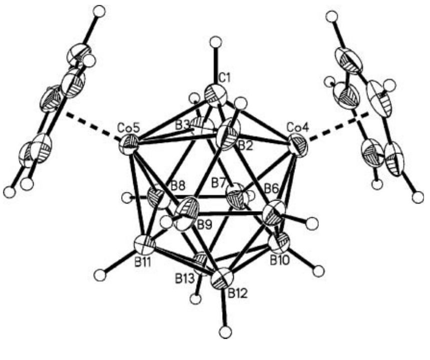


**Fig. 5** Perspective view of **5**. Vertices 6–9 are 75% B and 25% C but are labelled only as B for clarity. Average distances (Å) are C1–B2, C1–B3 1.512(7); B/C6–B/C9, B/C7–B/C8 1.755(7).

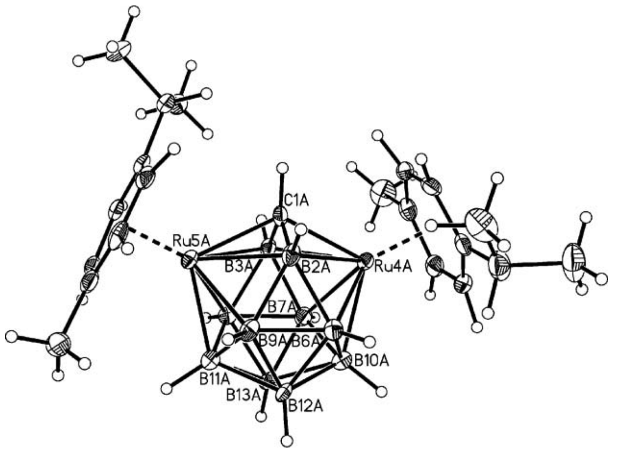
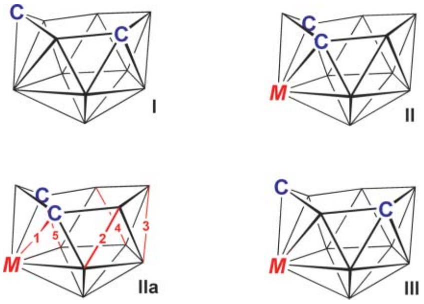


**Fig. 6** Perspective view of **6** (molecule A). As with **5**, vertices 6–9 are 75% B and 25% C but are labelled only as B for clarity. Average interatomic distances (Å, over both molecules): C1–B2, C1–B3 1.547(5); B/C6–B/C9, B/C7–B/C8 1.760(10).

dsd steps in which the red connectivities shown in **IIa** are sequentially broken. This affords **III**, which gives rise to **5** or **6** on metallation.



Two further species are formed in trace amounts along with **4** and **5** and have been characterised. Compound **7** is 3,6-$Cp_2$-3,6,1,2-*closo*-$Co_2C_2B_8H_{10}$, a known species[19] but not previously crystallographically characterised.‡ Compound **8** is also a 12-vertex biscobaltacarborane, the known species 2,3-$Cp_2$-2,3,1,7-*closo*-$Co_2C_2B_8H_{10}$.[20]

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## Notes and references

‡ Crystal data: for **1**: $C_{12}H_{25}B_9Ru\cdot CHCl_3$, $M = 487.05$, monoclinic, $P2_1/c$, $a = 9.6764(6)$, $b = 9.6037(5)$, $c = 22.9526(11)$ Å, $\beta = 101.127(3)°$, $V = 2092.9(2)$ Å$^3$, $Z = 4$, $D_c = 1.546$ Mg m$^{-3}$, $\mu = 1.127$ mm$^{-1}$, $F(000) = 976$. Data to $\theta_{max} = 43.45°$ collected at 100(2) K on a Bruker X8 diffractometer using Mo-$K_a$ radiation. 15490 out of 68251 independent reflections, $R_1 = 0.0397$, w$R_2 = 0.0686$, $S = 1.013$ for data with $I > 2\sigma(I)$.

For **2**: $C_{22}H_{39}B_9Ru_2$, $M = 602.96$, monoclinic, $P2_1/c$, $a = 17.6580(11)$, $b = 19.3688(12)$, $c = 15.7105(10)$ Å, $\beta = 110.117(3)°$, $V = 5045.4(5)$ Å$^3$, $Z = 8$, $D_c = 1.588$ Mg m$^{-3}$, $\mu = 1.208$ mm$^{-1}$, $F(000) = 2432$, $\theta_{max} = 33.77°$. 20092/176146 reflections, $R_1 = 0.0452$, w$R_2 = 0.0828$, $S = 1.011$, $I > 2\sigma(I)$.

For **4**: $C_{12}H_{21}B_9Co_2$, $M = 380.44$, monoclinic, $C2/c$, $a = 32.4745(17)$, $b = 7.8181(4)$, $c = 13.5715(7)$ Å, $\beta = 107.989(2)°$, $V = 3277.2(3)$ Å$^3$, $Z = 8$, $D_c = 1.542$ Mg m$^{-3}$, $\mu = 2.009$ mm$^{-1}$, $F(000) = 1536$, $\theta_{max} = 33.61°$. 6416/19685 reflections, $R_1 = 0.0391$, w$R_2 = 0.0778$, $S = 1.014$, $I > 2\sigma(I)$.

For **5**: $C_{12}H_{21}B_9Co_2$, $M = 380.44$, monoclinic, $C2/c$, $a = 28.838(3)$, $b = 8.7340(8)$, $c = 13.2705(12)$ Å, $\beta = 98.763(5)°$, $V = 3303.4(5)$ Å$^3$, $Z = 8$, $D_c = 1.530$ Mg m$^{-3}$, $\mu = 1.993$ mm$^{-1}$, $F(000) = 1536$, $\theta_{max} = 27.57°$. 3812/31203 reflections, $R_1 = 0.0356$, w$R_2 = 0.0816$, $S = 1.044$, $I > 2\sigma(I)$.

For **6**: $C_{22}H_{39}B_9Ru_2$, $M = 602.96$, monoclinic, $P2_1/c$, $a = 17.2154(14)$, $b = 20.7396(17)$, $c = 15.0264(12)$ Å, $\beta = 109.026(3)°$, $V = 5071.9(7)$ Å$^3$, $Z = 8$, $D_c = 1.579$ Mg m$^{-3}$, $\mu = 1.201$ mm$^{-1}$, $F(000) = 2432$, $\theta_{max} = 27.27°$. 11227/56146 reflections, $R_1 = 0.0328$, w$R_2 = 0.0625$, $S = 1.003$, $I > 2\sigma(I)$.

For **7**: $C_{12}H_{20}B_8Co_2$, $M = 368.62$, monoclinic, $P2_1/c$, $a = 6.7132(6)$, $b = 12.1272(10)$, $c = 18.2031(15)$ Å, $\beta = 90.153(4)°$, $V = 1482.0(2)$ Å$^3$, $Z = 4$, $D_c = 1.652$ Mg m$^{-3}$, $\mu = 2.220$ mm$^{-1}$, $F(000) = 744$, $\theta_{max} = 37.67°$. 7369/52192 reflections, $R_1 = 0.0247$, w$R_2 = 0.0599$, $S = 1.076$, $I > 2\sigma(I)$.

CCDC 640207–640212. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703822d

§ E.s.d.s of the mean of $N$ independent observations given by the expression $\sigma^2 = (\sigma_1{}^2 + \sigma_2{}^2)$ for $N = 2$, and $\sigma^2 = \{\Sigma_{i=1}^{i=N}(\chi i - \bar{\chi})^2\}/(N - 1)$ where $\chi i$ is the $i$th and $\bar{\chi}$ the mean value for $N > 2$.

¶ Calculations run with Gaussian 03 with the BP86 functional and 6-31G** basis sets. See ESI for full details.†

|| [4,5-$Cp^*{}_2$-6-$SMe_2$-4,5,2,3-*closo*-$Ru_2C_2B_9H_{10}$]$^+$, related to **3**, has also been reported by Kudinov *et al.*, although the structural study was relatively imprecise. Nevertheless the lengths of edges ***a***, 1.679(8), and ***b***, 1.843(13) Å, are comparable with those in **3**. See ref. 12.

** A similar crystallographic coincidence involving metallacarboranes has previously been observed. See ref. 16.

†† Three paramagnetic (13.5 SEP) 4,5,1,6,7-$Fe_2C_3B_8$ compounds of similar structure to the 14 SEP **5** and **6** have been reported by Štíbr and co-workers.[10] In **5** and **6** the average of six C1–B distances is 1.535(19) Å. In the Štíbr compounds the average of six C1–B distances is 1.563(6) Å. This lengthening may again be understood in terms of the nature of the HOMO of $[B_{13}H_{13}]^{2-}$, only half occupied in the ferracarboranes.

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